

STUDIES OF CO OXIDATION ON Pt/SnO₂ CATALYST IN A SURROGATE
CO₂ LASER FACILITY

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SUMMARY

Samples of 1% Pt/SnO₂ catalyst were exposed to a stoichiometric gas mixture of 1% CO and 1/2% O₂ in helium over a range of flowrates from 5 to 15 sccm and temperatures from 338° to 394° Kelvin. Reaction rate constants for the catalytic oxidation of carbon monoxide and their temperature dependence were determined and compared with previous literature values.

INTRODUCTION

Space-born, high-energy, pulsed laser systems are valuable for improved world-wide weather forecasting and for the more efficient operation of aircraft (ref. 1). They can measure wind velocity, temperature, and humidity at various levels in the atmosphere (refs. 1 and 2). They are also useful for measuring atmospheric pollutants, such as NH₃ and HCl (ref. 3). In this regard, the CO₂ TEA laser is of particular interest because of its high power, and, when used with rare isotope CO₂, such as C¹⁸O₂, its capability of improved atmospheric transmission (ref. 4).

For satellite applications the CO₂ laser must be operated closed-cycle to conserve gas, especially if rare isotope CO₂ is used. However, the laser discharge causes a dissociation of CO₂ into CO and O₂; in a short time period (10 to 20 minutes) a build-up of a small concentration of O₂ occurs. This causes a rapid power loss, ending in erratic behavior (ref. 4). To correct this problem, an efficient, low temperature catalyst is needed to recombine CO and O₂ to maintain a constant, high power level for long time periods (a year or more). For efficient laser operation, it should have high activity between 25 and 100°C at low concentrations of O₂ (<1/2 mol %).

Stark and Harris (ref. 5) formulated Pd/SnO₂ and Pt/SnO₂ catalysts that were found useful for the catalytic oxidation of CO. They observed a first order rate law for the conversion of O₂ and CO that fitted their data well; that is,

$$-\ln (p/P_0) = A \text{ wt}/V$$

where p is the partial pressure of oxygen at time t (sec), P_0 is the initial oxygen partial pressure, w is the catalyst mass(g), V is the volume of the test gas vessel (ℓ), and A is the volumetric pumping speed for the removal of O₂ (ℓ s⁻¹g⁻¹). A was treated like a reaction rate constant in an Arrhenius equation; that is,

$$A = B \exp (-E/RT)$$

$$\text{or } -\ln A = -\ln B + E/RT$$

where B is the pre-exponential ($\text{l s}^{-1}\text{g}^{-1}$), E is the activation energy, kJ mol^{-1} , R is the gas constant $8.31 \times 10^3 \text{ kJ mol}^{-1} \text{ }^\circ\text{K}^{-1}$, and T is absolute temperature, $^\circ\text{K}$. They found an E of 40 kJ mol^{-1} for the Pd/SnO_2 catalyst and 41 kJ mol^{-1} for Pt/SnO_2 catalyst.

Miller et al. (ref. 6) also observed a first order rate law for the conversion of CO and O_2 in a stoichiometric mixture of $1\% \text{CO} + 1/2\% \text{O}_2$ in He flowing through a $1\% \text{Pt/SnO}_2$ catalyst bed, or

$$-\ln (p/P_0) = k \tau$$

where k is the reaction rate constant (sec^{-1}) and τ is the contact time (sec) of the flowing gas in the catalyst bed. Then, using the Arrhenius equation

$$k = B \exp (-E/RT)$$

$$\text{or } -\ln k = -\ln B + E/RT$$

where B is the pre-exponential term (sec^{-1}) they found an E of 24 kJ mol^{-1} (ref. 7). That investigation was carried out at temperatures between 25 and 75°C . Data at higher temperatures were not useful because catalyst activity and sample size ($\sim \text{lg}$) resulted in O_2 conversion approaching 100 percent.

The purpose of the current study was to extend the temperature range by using a smaller sample size and to study the effect of varying the gas flowrate and catalyst temperature on the conversion efficiency of $1\% \text{Pt/SnO}_2$ catalyst which had been preconditioned more rigorously than that cited in reference 6.

In the previous study, the pretreatment conditions were very moderate compared to more rigorous pretreatment procedures developed subsequently in our laboratory. Specifically, in the previous study, one hour pretreatment with helium at 225°C was used, whereas more recent studies have shown that extending the pretreatment time to about 20 hours at the same temperature improved the stability of the catalytic reaction. Therefore, it was felt necessary to re-evaluate the catalyst under the more rigorous pretreatment conditions over a wider temperature range. Consequently, experiments were conducted to determine the activation energy and reaction rate constant of the catalytic oxidation of carbon monoxide and compare them with those obtained from the previous study. Additionally, since the catalyst is being evaluated for space applications, the weight of the catalyst is an important consideration. Therefore, we designed our tests so as to obtain the efficiency of the catalyst per unit weight of catalyst in order to determine the minimum amount of catalyst required for maximum efficiency under various conditions of temperature and gas flowrates.

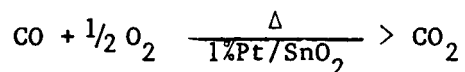
EXPERIMENTAL MATERIALS AND METHOD

The catalyst is a powder consisting of one percent platinum on tin oxide (w/w) which was prepared commercially by the method of Croft and Fuller (ref. 8). By that method, it was calcined at 450°C for five hours, then reduced with a mixture of 30 percent carbon monoxide in argon for two hours at 150°C . The catalyst parameters are shown in figure 1.

A weighed amount of catalyst was loaded into a plug-flow reactor which consists of a 6.8 mm I.D. quartz tube with stainless steel fittings at each end. The sample was held in place by quartz wool plugs as shown in figure 2. The loaded reactor was placed in a controlled temperature oven with stainless steel connections to the reactant gas mixture at the inlet and to the gas chromatograph at the outlet. A schematic of the entire surrogate laser facility is shown in figure 3.

As indicated in figure 1, the catalyst was pretreated for a period of 20 hours by passing high purity helium which has been dried with magnesium perchlorate and heating the reactor tube at 225°C, then cooled to room temperature under helium flow before starting the tests. The reactant stoichiometric gas mixture was first directed through a by pass line outside the oven to the gas chromatograph to measure the concentration of CO and O₂ at the inlet of the reactor. The test gas mixture contained 1% CO, 0.5% O₂, 2% Ne in helium. The neon served as an internal standard. This mixture was also passed through magnesium perchlorate to remove any water present.

The reactor was heated to the test temperature and the test gas mixture was passed through the catalyst bed at the selected flowrate. The product gases were sampled with a computer-actuated valve in the gas chromatograph which was programmed to sample consecutively for the first hour of testing and then at 90 minute intervals for the remainder of the test period. As indicated in figure 1, the chromatograph uses a coaxial column that has silica gel in one and molecular sieve in the other operated at 80°C. The coaxial column was used to separate the product components and a thermal conductivity detector was used for their measurement. The computer calculated the outlet/inlet ratios and printed the percent yield of CO₂, percent loss of O₂ and percent loss of CO for each sampling sequence. The reaction rate constant of CO and O₂ at the catalyst surface for the reaction



was determined by plotting the negative natural logarithm of the ratio of the partial pressure of oxygen in the product gas to that of the reactant gas at the inlet as a function of residence time. By using a plot of the logarithm of the reaction rate constant versus reciprocal absolute temperature, the activation energy and pre-exponential values were determined.

TESTS

Two series of tests were conducted as outlined in figure 4. During the first series, the temperature and gas flowrate were held constant at 100°C and 10 sccm, respectively, while samples of different weight were tested. This enabled the determination of the amount of catalyst that was required for complete conversion, or 100 percent CO₂ yield, and to select the size sample for the next series of tests.

For the second series of tests samples of catalyst weighing 0.15 gram (so as to remain below 100 percent conversion) were exposed to the tests gas flowing at 5, 10, or 15 sccm while the temperature was ramped up or down from 55°C to 120°C. Fresh catalyst samples were used for each flowrate condition, each pretreated with helium prior to testing. While data were collected from the beginning of the test, only the data that were obtained after the reaction reached steady state conditions were used for the analysis, usually between 1000 and 4400 minutes.

RESULTS

The results of the first series of tests are shown in figure 5. The CO₂ conversion efficiency increased linearly with increase in catalyst sample mass and approached 100 percent with a catalyst mass of approximately 0.17 gram under constant temperature and flowrate. Based on these results, a catalyst sample of 0.15 gram was selected for the next series of tests so as to vary the flowrate and temperature without reaching the 100 percent CO₂ conversion.

The decay of oxygen in the product gas as a function of temperature for 3 different constant flowrate conditions of 5, 10 and 15 sccm is shown in figure 6. On increasing the temperature and returning to the initial temperature condition, no significant hysteresis was found within experimental error.

The reaction rate constants for the various temperature levels are shown in figure 7. The data suggest a first order reaction, which is consistent with the data obtained by Stark and Harris (ref. 5) and Miller et al. (ref. 6). The dependence of the rate constants on temperature is shown in figure 8. A correlation coefficient of .9972 was obtained. Calculations from this graph yielded an activation energy, $E = 55 \text{ kJ mol}^{-1}$ and a pre-exponential, $B = 7.5 \times 10^7 \text{ sec}^{-1}$.

DISCUSSION

In order to compare the data in the literature with that in the current study, it is necessary to convert all the data to the same basis, that is, the data need to be normalized. The key parameter that needs to be normalized is the pre-exponential factor B, in the Arrhenius equation:

$$k = B \exp (-E/RT)$$

where k = the reaction rate constant, sec^{-1}
 B = pre exponential factor, sec^{-1}
 E = activation energy, kJ mol^{-1}
 R = Universal Gas Constant, $\text{kJ mol}^{-1} \text{ } ^\circ\text{K}^{-1}$
 T = Absolute temperature $^\circ\text{K}$

By normalizing B, k is also normalized. The value of k found in the present study, as well as that found by Miller et al. is given in the dimension of sec^{-1} , whereas a similar parameter reported by Stark and Harris, which they call A, the pumping speed, is given in the dimension $\text{l gm}^{-1} \text{ sec}^{-1}$.

A reaction rate constant that would be common to all three sets of data is k' , in the dimension $\text{sec}^{-1} \text{ gm}^{-1}$. To convert the B and k values in the present study, as well as those in the study by Miller et al, requires division of B and k , by the sample weight used, w , in gms, or $k' = k/w \text{ sec}^{-1} \text{ gm}^{-1}$ and $B' = B/w \text{ sec}^{-1} \text{ gm}^{-1}$. The value of w in the current study is 0.15 grams and the value of w reported by Miller et al. is 0.925 grams.

To convert the pumping speed, A, reported by Stark and Harris to k' , it is necessary to divide their A value by the volume of the test gas vessel, V, which is 1.2 l, or

$$k' = \frac{A}{V} \text{ gm}^{-1} \text{ sec}^{-1}$$

The pre-exponential, B' , was calculated from the Arrhenius equation using their reported activation energy of 41.4 kJ mol^{-1} and several k' , T values. The average B' value was $1609 \text{ sec}^{-1} \text{ gm}^{-1}$.

However, Stark and Harris used a 1.3% Pt loading on SnO_2 , whereas Batten and Miller et al. used a 1% Pt loading on SnO_2 . To make the k' values of Stark and Harris comparable, it was assumed that catalyst activity was proportional to platinum loading. Therefore, the B' value of 1609 was divided by 1.3 to obtain an adjusted B' value of $1238 \text{ sec}^{-1} \text{ gm}^{-1}$. The values of B' and E in the Arrhenius equation used to calculate the K' values for all three studies are as follows:

Reference	Pre-exponential	Activation Energy	Temperature Range,
	$B', \text{ sec}^{-1} \text{ gm}^{-1}$	$E, \text{ kJ mol}^{-1}$	$^{\circ}\text{C}$
Current Study	5×10^8	55.0	65-121
Miller et al.	1690	24.0	25-75
Stark and Harris	1238	41.4	21-60

Values of k' versus $1/T$ are plotted in figure 9 for all three studies. Note that the k' values of this study are about an order of magnitude greater than those of Miller et al. Even though aliquots of the same catalyst were used in both studies, in Miller et al. an aliquot was taken from the top end of the initial sample shortly after receipt from the manufacturer. In three years, this sample was drawn down for other studies, so that aliquots taken for the current study represent portions taken from the bottom end of the sample. When there is a mixture of particles of the same density but of different size, the smaller particles will settle to the bottom of the mixture. Therefore, aliquots of the sample used in the present study will probably have a particle size distribution with a smaller mean particle size than in the earlier study. A smaller mean particle size may be associated with a higher surface area and higher Pt loading and may result in higher k' values. Another reason for the higher k' values in the current study is, probably, the more rigorous pretreatment given the catalyst compared to that in the other study. In the other study, the catalyst was pretreated with flowing He at 225°C for one hour. In the present study the catalyst was pretreated with He at 225°C for 20 hours. Previous studies had shown that this extended pretreatment time increased catalyst activity. The effect of catalyst aging during the three year time interval between the two studies is unknown.

Also, in figure 9, the k' values of Stark and Harris are several orders of magnitude below those of the present study. There may be several reasons for these low k' values. The catalyst granules were spread thinly over an area of about 15 cm^2 at the base of the laser envelope. Although no mention was made of gas circulation in the envelope, even if there were good circulation, contact of the gas mixture with the granules would not be as effective as if the granules were in a bed through which the gas mixture flowed. In this case, mass transfer would be limited mostly to diffusional processes rather than by momentum transfer. Furthermore, no mention was made of any preconditioning of the catalyst as was done in the other two studies. Preconditioning has been shown to have a very beneficial effect on catalyst activity. Finally, Stark and Harris used a gas mixture of 31% CO_2 , 16% N_2 , 43% He, 7% CO and 3% O_2 . The concentration levels of CO and O_2 in their study are considerably higher than in the current and the previous study where gas mixtures of

1% CO and $\frac{1}{2}$ % O₂ in He were used. The effect of higher concentrations of CO and O₂ on the activity of the Pt/SnO₂ catalyst is unknown and would have to be determined by kinetic studies.

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A. Catalyst - 1% Pt/SnO₂ in plug-flow reactor B. Test gas

Stoichiometric mixture:

- 1% CO, 1/2% O₂, 2% Ne, in He

Parameters:

- Average particle size - 1 μ m
- Bulk density - 1.934 g/cm³
- SnO₂ density - 7.0 g/cm³
- BET area - 6.9 m²/g
- Specific void volume:

$$V'_0 = \left(\frac{1}{1.934} - \frac{1}{7.0} \right) = .374 \text{ cm}^3/\text{g}$$

C. Analytical method

Gas chromatography:

- Column type - coaxial column
silica gel/molecular
sieve
- Column temperature - 80°C
- Column flowrate - 40 Sccm

Pretreatment:

- 20 hrs at 225°C with helium gas

Figure 1. Experimental materials and method.

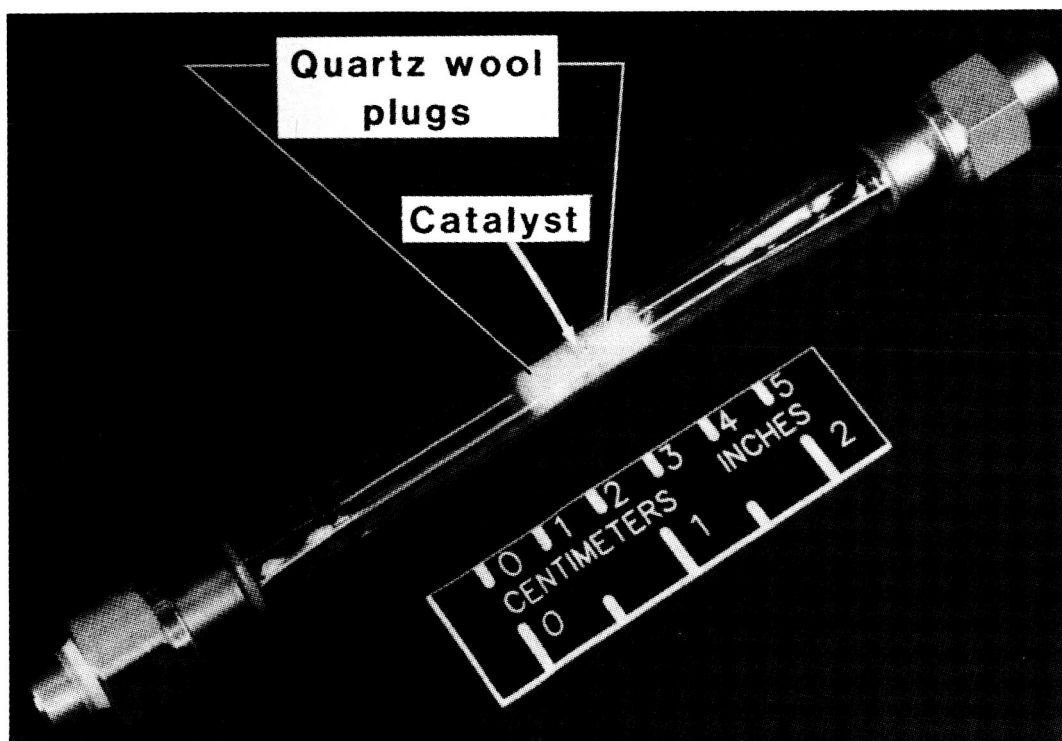


Figure 2. Catalyst reactor.

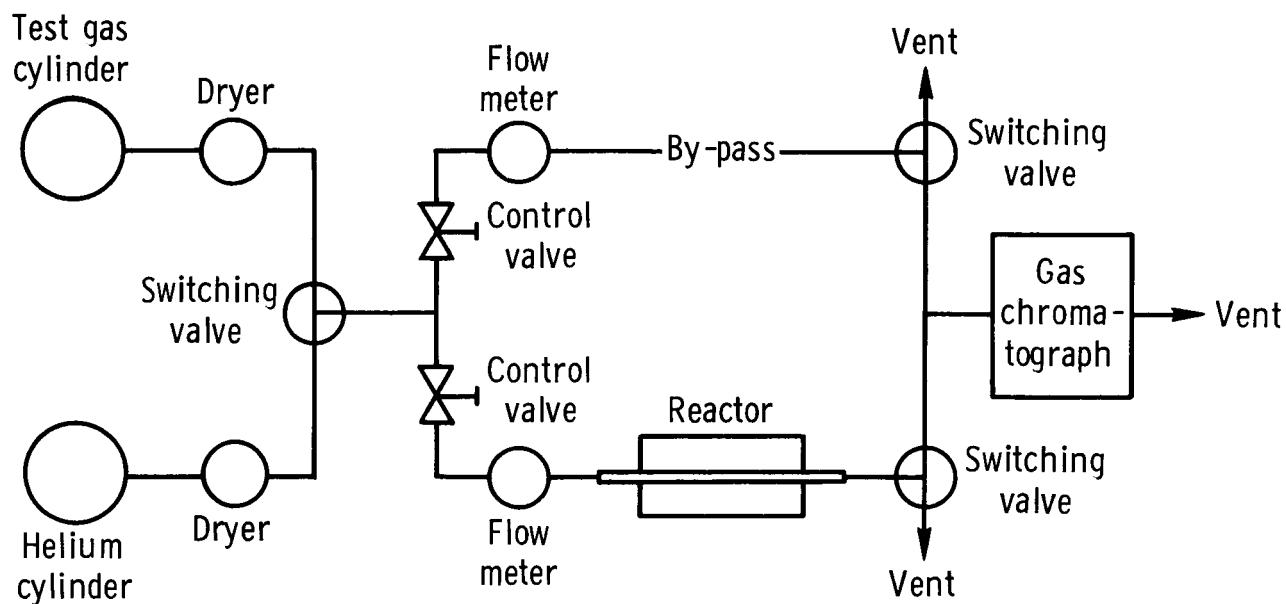
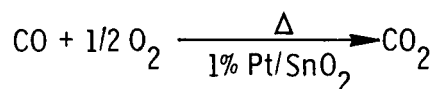


Figure 3. Schematic of surrogate laser facility.



- Test 1 - Constant temperature - 100°C
Constant flowrate - 10 Sccm
Varying catalyst mass - 0.06 - 0.24g
- Test 2 - Constant catalyst mass - 0.15g
Test gas flowrates - 5, 10, 15 Sccm
Reactor temperatures - 55°C - 120°C

Data obtained	Data calculated
% yield CO ₂	Reaction rate constants (sec ⁻¹)
% loss O ₂	Activation energy - (kJ mol ⁻¹)
% loss CO	Pre-exponential (sec ⁻¹)

Figure 4. Reaction rate measurements.

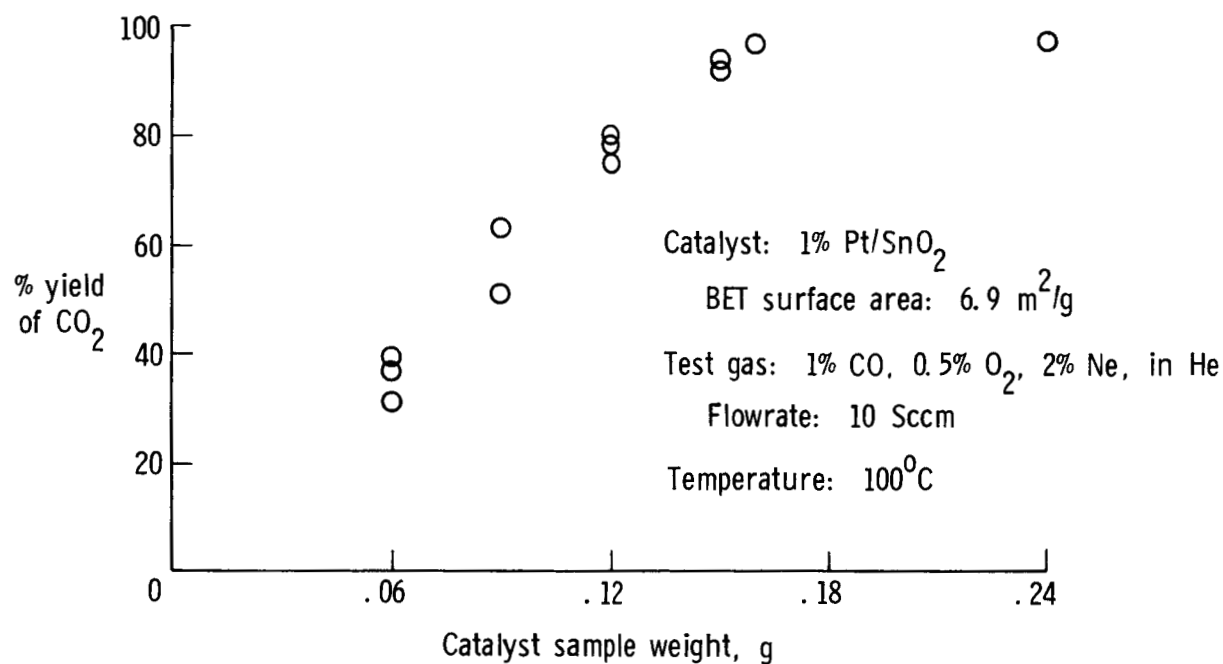


Figure 5. Conversion efficiency of catalyst versus sample weight.

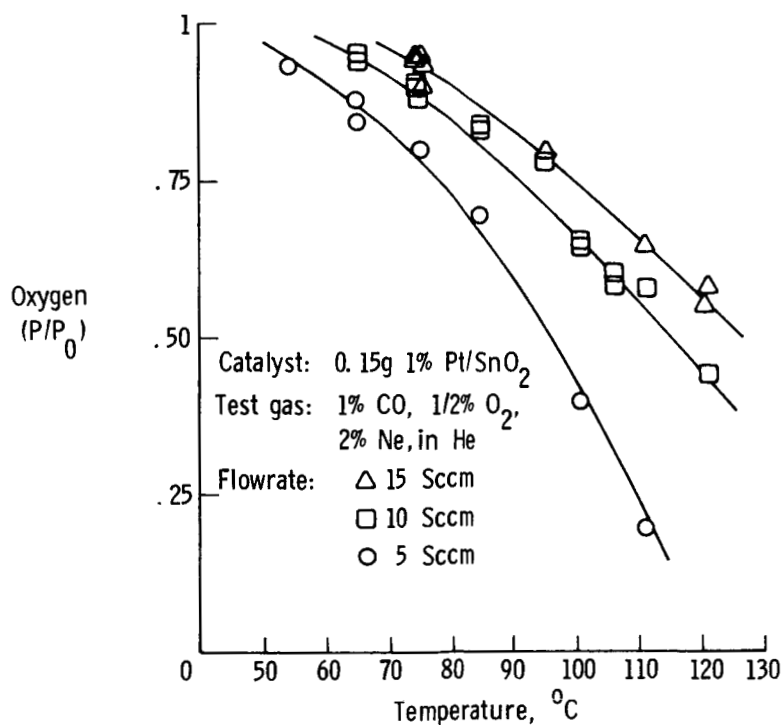


Figure 6. Reaction rates for constant reactant concentrations.

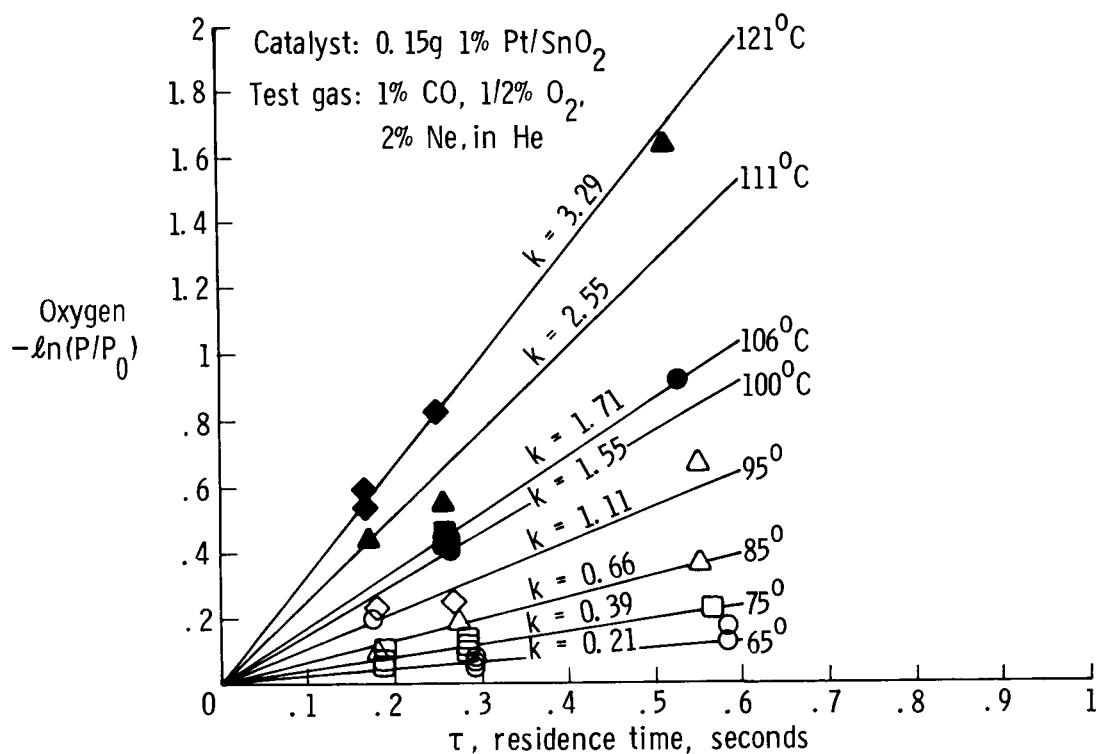


Figure 7. Reaction rate constants, k .

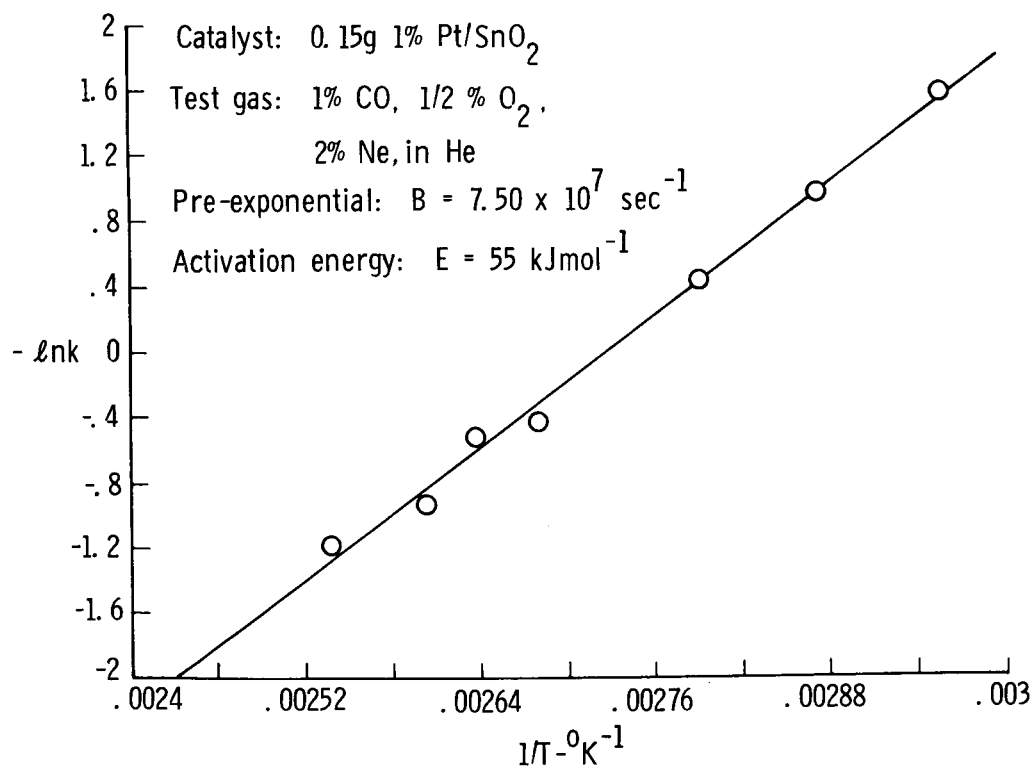


Figure 8. Arrhenius plot.

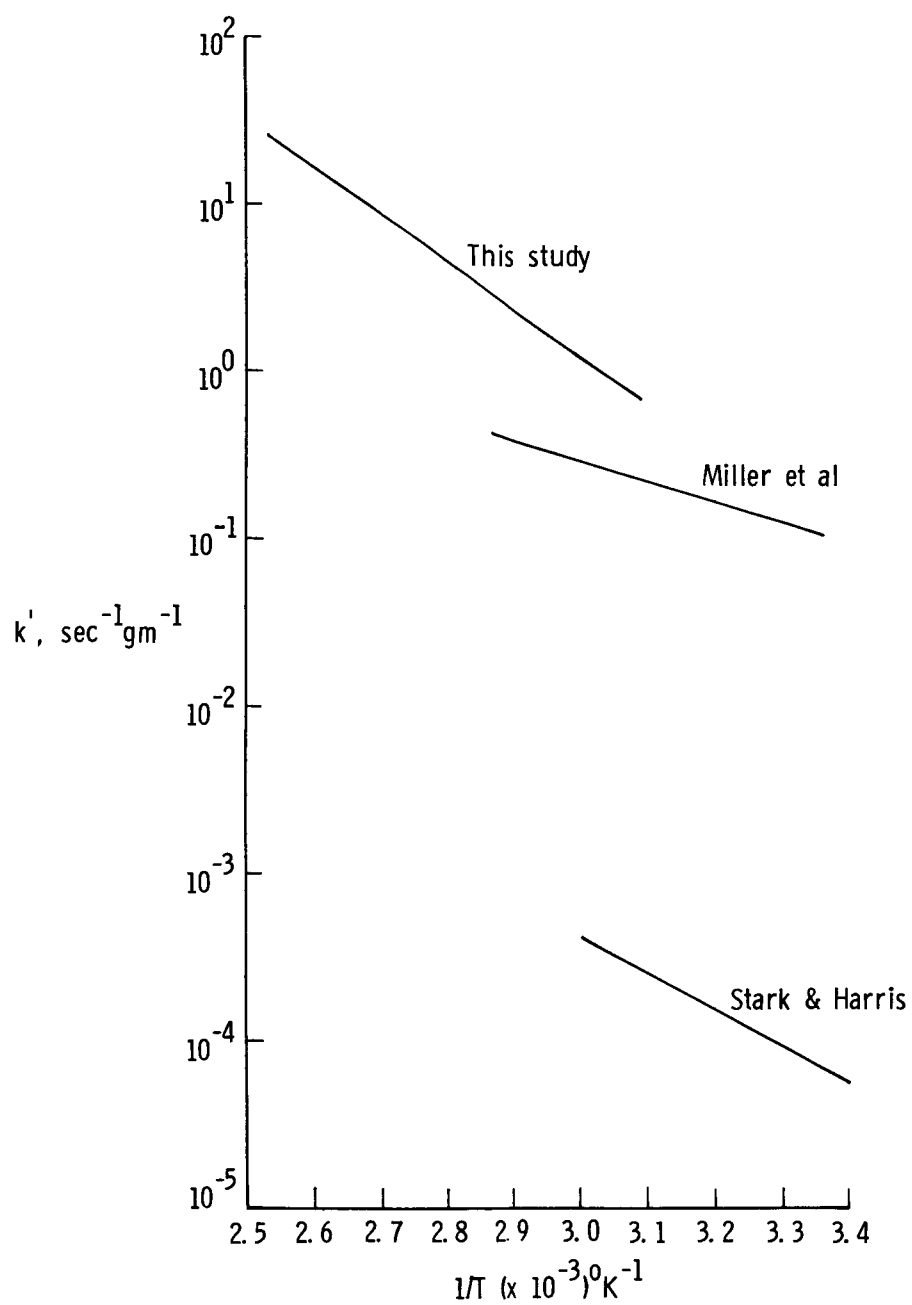


Figure 9. Plots of the Arrhenius equation for CO oxidation on Pt/SnO₂ catalysts.